

QUANTITATIVE MEASUREMENTS OF CO CONCENTRATIONS IN LAMINAR AND TURBULENT FLAMES USING TWO-PHOTON LASER-INDUCED FLUORESCENCE

GREGORY J. FIECHTNER

Innovative Scientific Solutions, Inc.
2766 Indian Ripple Road, Dayton, OH 45440-3638
E-mail: gjfiech@ward.appl.wpafb.af.mil

CAMPBELL D. CARTER

Innovative Scientific Solutions, Inc.
2766 Indian Ripple Road
Dayton, OH 45440-3638

ROBERT S. BARLOW

Combustion Research Facility
Sandia National Laboratories
Livermore, CA 94551-0969

ABSTRACT

Laser diagnostics can provide nonintrusive measurements of the instantaneous velocities and species concentrations, and statistical information from such measurements may be used to evaluate modeling approaches for turbulent nonpremixed combustion. An important flame constituent in these studies is carbon monoxide. Numerous studies have been performed in turbulent flames using single-shot Raman scattering measurements, despite extremely small optical scattering cross sections, which require the use of high-energy laser pulses. In the presence of hydrocarbons, high-energy laser pulses cause interfering light, for instance from emission due to laser-produced C_2 . In this study, we examine concentration measurements of CO using two-photon, laser-induced fluorescence (TPLIF). Excitation of the $X^1\Sigma^+-B^1\Sigma^+$ transition of CO is attempted because laser photons can also photoionize the excited state. The photoionization rate can help make TPLIF detection of CO quantitative. This is examined in several laminar and turbulent flames by direct comparison with simultaneous Raman measurements of CO concentration. Excellent agreement is observed for a number of laminar flame conditions. Disappointing results are obtained in turbulent CO/ H_2/N_2 jet flames. Reasons for the anomalous results are explored.

INTRODUCTION

Carbon monoxide is an important molecule in hydrocarbon combustion processes, and the accurate and precise determination of CO concentrations is important in many studies of combustion, including propulsion, power generation, and other processes that utilize combustion in their operation.

Our own interest lies in the rigorous testing of turbulence combustion models within the collaborative framework of the International Workshop on Measurement and Computation of Turbulent Nonpremixed Flames (Barlow, 1996). Here, detailed experimental data sets are obtained and then provided to modelers for comparison with their computed results. To this end, the effects of turbulent mixing on reaction-zone structure have important implications for combustion models, and a more complete understanding of the response of species mass fractions is needed.

Previous experimental studies of CO concentrations in piloted and bluff-body stabilized flames of various fuels have yielded notable results. CO levels measured by Raman scattering in piloted flames of undiluted methane were significantly higher than those calculated in laminar flames (Chen et al., 1989). Rayleigh/Raman measurements in bluff-body flames of methane reported by Masri et al. (1992) and Correa and Gulati (1994) have also shown CO levels higher than those from laminar flame calculations and PDF model predictions. Computational studies have been conducted to investigate mechanisms that might contribute to the high measured levels of CO. Mauß et al. (1990) considered effects of unsteadiness on laminar flames and suggested that high CO concentrations result from an extinction-reignition process. Chen and Dibble (1991) observed that high CO levels are also observed in perfectly-stirred reactor calculations.

Despite these previous results, many potential future observations of CO behavior in these burners hinge on the limitations of the Raman scattering technique: because of the low optical cross section for Raman scattering, large laser-energy density is required; in our own laboratory as much as

2.4 J (at 532 nm) is focused into a spot size of approximately 800 microns. In flames with an appreciable hydrocarbon content, this high energy density can photolytically produce light that interferes with the detection of Raman photons scattered from CO. As part of a Raman instrument, a detector is reserved to collect broadband fluorescence interferences, and an attempt is then made to use the interference channel to correct the CO signals. Unfortunately, it is often impossible to correct the CO Raman signal and obtain useful data, for example in some nonpremixed methane-air flames (Correa et al., 1994).

Because of these difficulties, we are continually seeking different approaches to measure carbon monoxide. A promising technique is two-photon laser-induced fluorescence (TPLIF). Recently, Everest et al. (1996) measured CO using TPLIF in a periodically forced, laminar, rich ethylene-air flame. Background interference due to laser-induced incandescence from soot particles, broadband fluorescence from polycyclic aromatic hydrocarbons, and laser-induced production of C₂ Swan-band emission was detected by tuning the excitation slightly off resonance, and repeating the measurement to correct the on-resonance LIF signal. In this manner, CO concentration measurements were found to be of value even when soot volume fractions up to 5 ppm were present. In this manuscript, we describe experiments in which the TPLIF technique is tested as a means of quantitatively measuring CO concentrations on a single-shot basis in turbulent flames. Direct comparisons are made with simultaneous Raman measurements of the CO concentration. In some cases, the use of TPLIF is found to characterize the CO concentration adequately. There is, however, one case in which the agreement is unacceptable. This case is analyzed, and possible reasons for discrepancies are discussed.

BACKGROUND

A widely applied optical diagnostic is laser-induced fluorescence (LIF), because its favorable signal-to-noise ratio allows detection of even minor flame constituents. Because of the large energy separation between the ground and excited electronic levels of CO, LIF measurements require two-photon excitation. Nevertheless, a number of studies have indicated that LIF detection of CO using two-photon excitation of the X¹Σ⁺–B¹Σ⁺ transition, followed by fluorescence detection from the B¹Σ⁺–A¹Π transition, may be a viable diagnostic in turbulent hydrocarbon flames. Using this method, Aldén et al. (1984) achieved a detection limit for CO of 200 ppb in a cell. In premixed laminar methane-air flames and a highly turbulent propane-air flame, Aldén et al. (1984) observed background emission from the laser production of C₂ radicals that emitted light, interfering with the emission from the B¹Σ⁺–A¹Π levels. They proposed that spectral filtering could remove most of this interference. The resulting signal level was sufficient for single

shot detection in their turbulent flames. In addition, Aldén et al. (1984) used a linear array and captured line images of flames. Hauman et al. (1986) and Seitzman et al. (1987) used the technique to collect single shot, two-dimensional images in an unsteady, premixed methane-air flame. They also encountered laser-produced C₂ that emitted light, interfering with the CO emission. In some of their measurements, the investigators found that a 10-nm bandpass filter centered at 486 nm could isolate the (0,1) band of the B¹Σ⁺–A¹Π fluorescence and reject much of this background. For their system, a single-shot detection limit of 4.9×10¹⁵cm⁻³ was reported at 1900 K in a laminar, methane-air diffusion flame without the bandpass filter.

Reduction of Quenching Effects by Photoionization

The LIF signal is proportional to the number density of molecules N₂ that are excited by absorption of photons from the resonant laser. This can be expressed as (Lucht, 1987),

$$N_2 = \frac{N_T W_{12}}{Q + A_{21}}, \quad (1)$$

where N_T is the total number density (m³) of the species in question, Q is the quenching rate (s⁻¹), A₂₁ is the rate for spontaneous emission (s⁻¹), and W₁₂ (s⁻¹) is the rate for absorption. Fluctuations in the collisional environment can cause uncertainty in the LIF signal because of the rate Q in the denominator of Eq. (1). For molecules undergoing two-photon excitation, the excited state has an energy close to that of the ionization threshold. Salmon and Laurendeau (1990) applied this principle during TPLIF excitation by sending a second laser through the test section. Photons from the second laser are absorbed by excited-state molecules, promoting them to the ionization continuum. For this process, which Salmon and Laurendeau (1990) called “photoionization-controlled loss spectroscopy” (PICLS), Eq. (1) is modified to take the form

$$N_2 = \frac{N_T W_{12}}{Q + A_{21} + W_{\text{ion}}}, \quad (2)$$

where W_{ion} represents the photoionization rate (s⁻¹). The irradiance of the photoionization laser beam is chosen to be large enough to satisfy the condition W_{ion} >> Q, so that fluctuations in the collisional environment become negligible. Unfortunately, for comparatively large values of Q, this also means that the denominator of Eq. (2) is large, and the TPLIF signal is therefore small. Hauman et al. (1986) and Seitzman et al. (1987) proposed a TPLIF technique that, like the PICLS technique, relies on photoionization of the excited state, but relies on only one laser for both two-photon absorption and photoionization. As noted by Hauman et al. (1986) and Seitzman et al. (1987), the technique works well for TPLIF excitation of the X¹Σ⁺–B¹Σ⁺ transition of CO with a laser of wavelength near 230 nm, because the energy of laser photons is adequate to then photoionize the excited state. Because all

three photons come from a single laser, the rates for two-photon absorption and one-photon photoionization can be directly related by their dependence on the laser irradiance, based on the expressions

$$W_{ion} = \frac{\sigma_{ion} I_L}{h c \nu_L}, \quad (3)$$

and

$$W_{12} = \frac{\alpha_{12} I_L^2}{h c \nu_L}. \quad (4)$$

Here, h is the Planck constant (J·s), c is the speed of light (m/s), ν_L is the laser frequency (s^{-1}), and I_L is the laser irradiance (W/m^2). In addition, σ_{ion} represents the photoionization cross section (m^2), and α_{12} (m^4/W) is a quantity proportional to the integrated two-photon absorption cross section, which has units of m^4 (Bamford et al., 1986; Saxon and Eichler, 1986). From Eqs. (2), (3), and (4), it is clear that for infinitely small values of laser irradiance, $W_{ion} \ll Q$, and N_2 will be proportional to $I_L^2/(Q+A_{21})$, whereas for infinitely large values of laser irradiance, $W_{ion} \gg Q$, and N_2 will be proportional to I_L . Therefore, for large values of laser irradiance, the signal will have a reduced dependence on collisional quenching fluctuations. Moreover, the technique has a distinct advantage over the PICLS method in that the signal continues to increase as the quenching-independent regime is approached. Assuming the photoionization-controlled limit applied for their experiments, Hauman et al. (1986) and Seitzman et al. (1987) found that their TPLIF measurements of CO concentration agreed with sampling probe measurements to within a maximum discrepancy of approximately 20% along the centerline of a CO-air diffusion flame.

Irradiance-Dependent Exponent

Consider the TPLIF signal, which is proportional to the excite-state population, N_2 , to in turn be proportional to the laser irradiance raised to an exponent, b , such that

$$N_2 \propto I_L^b. \quad (5)$$

Comparing with Eqs. (2), (3), and (4), it is apparent that in the limit of small irradiance, $b=2$, and for large irradiance, $b=1$. In principle, it should be possible to determine the degree of photoionization by measuring the irradiance dependence of the CO TPLIF signal. This has been an underlying assumption during applications of the technique by a number of investigators. Hauman et al. (1986) and Seitzman et al. (1987) do not report an irradiance-dependence measurement in their work, instead citing a value of $b=1.2$ reported in low-pressure room temperature measurements by other investigators. Van Oostendorp et al. (1991) applied the technique with the assumption of the photoionization-controlled loss limit to line imaging in a commercial natural gas burner and a Bunsen flame using a power dependence of $b=1.2$. The investigators

examined laminar flames, with results averaged over numerous shots. Mokhov et al. (1995) studied single-shot CO TPLIF measurements in a turbulent nonpremixed bluff-body flame of natural gas and air. These investigators measured a power dependence $b=1.5$ and therefore ignored quenching variations. Everest et al. (1996) worked with an irradiance-dependent exponent near unity and were able to obtain sublinear irradiance dependencies in flames at higher irradiances.

Clearly, measurement of the irradiance-dependent exponent has been used to determine at which point the TPLIF process is in the photoionization-controlled limit, making it a quantity of critical importance to the technique. Unfortunately, the photoionization-controlled limit applies strictly in the limit of infinite laser irradiance, for which $b=1$. Practical values of laser irradiance will yield values of b that are greater than 1. In these cases, the photoionization-controlled limit will not completely apply, and the influence of quenching will only be partially reduced. To estimate this effect, first note that the irradiance-dependent exponent from Eq. (5) can be evaluated using the expression

$$b = \frac{\frac{dN_2}{N_2}}{\frac{dW_{ion}}{W_{ion}}}, \quad (6)$$

the right side of which we define as the irradiance-dependent operator. This quantity is equivalent to the exponential index that is frequently applied when considering multiphoton ionization processes (Eberly, 1979). Application of this operator to Eq. (2) yields the expression

$$b = \frac{2 + \frac{W_{ion}}{Q + A_{21}}}{1 + \frac{W_{ion}}{Q + A_{21}}}, \quad (7)$$

which approaches $b=2$ in the limit of small laser irradiance and $b=1$ in the limit of large laser irradiance. Intermediate laser irradiance results in values of the irradiance-dependent exponent ranging between 1 and 2. Having identified an expression for the irradiance dependence of the TPLIF signal, consider the influence of the signal on quenching, which can be evaluated from the expression

$$\frac{dN_2}{N_2} = (b-1) \frac{dQ}{Q + A_{21}}. \quad (8)$$

Hence, the dependence of the TPLIF signal on quenching varies linearly with the irradiance-dependent exponent. Any value of irradiance yielding a value of b between 1 and 2 will only partially reduce the dependence of the TPLIF signal on quenching. For example, if $b=1.5$, the dependence of the TPLIF signal on quenching will be reduced by only 50%. In

practice, nonlinear absorption processes such as two-photon excitation depend heavily on other factors such as the temporal and spatial distribution of laser pulses (Wirth and Fatunmbi, 1990), so that Eq. (6) will not strictly apply, and specific conclusions regarding the magnitude of quenching reduction may be either underestimated or overestimated (Fiechtner and Barlow, 1999). Moreover, other research groups have found the CO TPLIF signal may be an unreliable measure of the concentration (Bernstein, 1991). Therefore, we have undertaken a study in which single-shot TPLIF signals are collected simultaneously with Raman measurements of the CO concentration.

APPARATUS AND PROCEDURE

An injection-seeded Quanta Ray DCR2-A Nd:YAG laser is frequency doubled to pump a PDL-2 dye laser with Kiton red dye in both the oscillator and amplifier stages. The dye output is frequency doubled, and the resulting light is mixed with the fundamental Nd:YAG laser output to produce light near 230.1 nm (a mean value of 700 μ J at the burner). A quartz plate is used to direct a portion of the light to a diffuser, followed by a photodiode. The photodiode output is directed to a Stanford Research Systems boxcar integrator, and the resulting voltage is collected to correct TPLIF signals for fluctuations of laser energy. These corrections are performed by directly dividing the signal by the value of laser irradiance, in contradiction to Eq. (5). No substantial improvement in signal-to-noise is achieved when including the value of b in the correction process. This results, in part, from the comparatively stable operation of the CO TPLIF laser system, which produces shot-to-shot irradiance fluctuations of approximately $\pm 4\%$ with a fresh batch of laser dye in the amplifier stage of the PDL-2 dye laser.

Before the beam enters the test section, some of the light is split off using a quartz plate at 45° and focused into a reference cell using a 100-mm focal-length lens. Gas consisting of 1% CO in helium, delivered from an aluminum cylinder, flows continuously through the cell at room temperature. Fluorescence is collected at right angles and directed through a 10-nm bandpass filter centered at 484 nm. Light is then detected using a photomultiplier with the anode directly integrated by an EG&G Ortec 142A amplifier, the output of which is directed to a Stanford Research Systems boxcar integrator with a 50-ns gate. The purpose of the cell is to track changes in laser wavelength.

Fluorescence collected at right angles to the laser path using a Cassegrain telescope is directed through a 10-nm bandpass filter, centered at 484 nm. Because of intense scattering of light from the Rayleigh/Raman laser system, a second filter with 25-nm bandpass, also centered at 484 nm, is

used to prevent damage to the detection electronics. Slits mounted in front of the photomultiplier define the axial collection volume length at approximately 400 microns. The photomultiplier output is directed to a Stanford Research Systems amplifier and then to a Stanford Research Systems boxcar amplifier/integrator with a gate width of 50 ns. The linearity of the detection system has been evaluated carefully and found to be approximately two decades.

For power-dependence studies, four quartz plates are used to vary the energy by placing them directly in the laser beam path. Before entering the test section, laser light is passed through a telescope to adjust the size and position of the focus above the burner. To examine the influence of the power dependence, b , and collection volume on the Raman/LIF comparison, two beam diameters are used. For large irradiance, the beam is focused to a diameter of approximately 260 μ m, which results in an irradiance dependence in our calibration burner between 1.2 and 1.4, depending on the age of the laser dye. For the small-irradiance, large-collection-volume case, the beam diameter is increased to greater than 800 μ m, resulting in an irradiance-dependent exponent of approximately 1.9.

LIF measurements of CO are made nearly simultaneously with measurements of the majority species (including CO) using Raman scattering, and temperature using both Rayleigh and Raman scattering. In addition, near simultaneous OH and NO LIF concentration measurements are performed using two additional laser systems. A detailed description of the Rayleigh/Raman/LIF instrument, along with the associated calibration procedure, is provided elsewhere (Nguyen et al., 1996; Barlow et al., 1996). The pulses from each laser system are delayed in time with respect to each other. The OH LIF laser pulse arrives in the flame first, followed after 100 ns by the NO LIF laser pulse. There are two laser pulses used for the Rayleigh/Raman system, with the first and second pulses delayed from the NO LIF pulse by 100 ns and 250 ns, respectively. The CO LIF laser pulse then arrives after the second Rayleigh/Raman laser pulse by 1.15 microseconds.

Temperature measurements are thus taken on a single shot basis along with corresponding single-shot TPLIF measurements of the CO concentration. The temperature measurements are used to correct for Boltzmann fraction changes, which in turn depend on the rotational levels excited by the laser (as determined by the reference-cell measurements). The Boltzmann fraction for a particular rotational level can be calculated using the partition function of Goorvitch (1994) that applies for temperatures up to 10,000 K, vibrational levels up to 41, and rotational levels up to 94. The spectroscopic calculation procedure is further described by Fiechtner et al. (1999).

The CO LIF system is calibrated using a flat flame "Hencken" burner (Hancock et al., 1997), which can be operated in a premixed or nonpremixed fashion. In addition, since both the Raman and TPLIF instruments are calibrated simultaneously in flames above this burner, comparisons of the results obtained with each instrument are also performed. Premixed methane/air flames and nonpremixed H_2/CO /air flames are supported. The equivalence ratio is varied from lean conditions to rich conditions, producing variation in both temperature and CO concentration. Single-shot pdf data obtained in turbulent flames require calibration of both the instrument sensitivity and the *spread* of the data about the calibration curve. This is accomplished by fitting the signal-to-noise ratio as a function of CO concentration. We define this ratio in terms of the Gaussian standard deviation. In a quiescent flow, the variation of the LIF signal is not well-described by a Gaussian distribution, with a majority of the points falling to the high end of the signal median. In their ion-imaging experiments, Nguyen and Paul (1996) have noticed a similar non-Gaussian distribution in shot-to-shot signal variation during two-photon excitation of hydrogen radicals in a quiescent reacting flow. Hence, we made a brief attempt to fit the variation in the signal-to-noise ratio with CO concentration using a skewed distribution function, but no substantial change in data interpretation was observed. Therefore, as a matter of convenience, we vary the confidence level using a Gaussian standard deviation so that confidence intervals contain the spread of the single-shot data about the calibration curve. These confidence intervals can then be plotted on scatterplots of data taken in turbulent flames. As the concentration of CO is decreased to some critically small value, even large fluctuations of concentration due to turbulence will be masked by instrument noise. Using the calibration for signal-to-noise ratio, we can estimate when the spread in a scatterplot caused by fluctuations in CO concentration is significant.

In addition to the laminar calibration flames, two turbulent burners also provide flames in which data are taken. The first case consists of a simple, attached, nonpremixed, jet flame of 40% CO, 30% H_2 , and 30% N_2 (also referred to as "syngas" in the literature). In addition to our interest in this flame for providing data sets that are useful for quantitative testing of turbulent combustion models (Barlow et al., 1999), it is also possible to obtain comparatively good-quality CO concentration data using Raman scattering, which is of critical importance in evaluating the potential of the TPLIF technique. The second case consists of a premixed, methane-air-fueled, bluff-body flame operated under lean and near-stoichiometric conditions. For comparison of Raman and TPLIF measurements of CO concentrations in these turbulent flames, data are plotted against the temperature derived from Rayleigh/Raman measurements.

RESULTS AND DISCUSSION

Typically, the Raman scattering channel and the TPLIF channel are calibrated separately using the known CO concentrations in the laminar flames. The results of one such

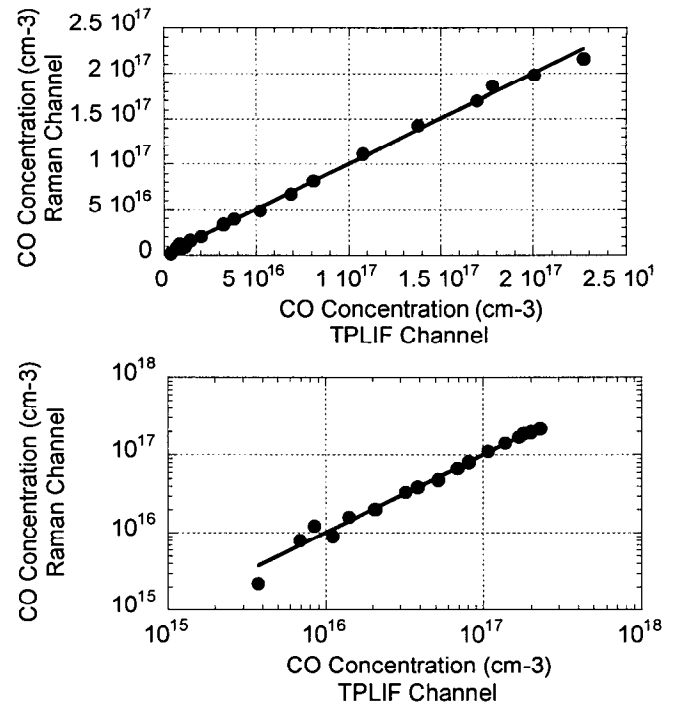


Figure 1. Calibrated TPLIF and Raman measurements of CO concentration plotted against each other on a linear (upper plot) and a log-log (lower plot) scale. The solid line is a linear least-squares fit.

calibration process are shown in Fig. 1, where the Raman scattering result is plotted against the corresponding TPLIF result using filled circles. A linear, least-squares fit is superimposed. The upper plot of Figure 1 contains a linear scale, while the lower plot contains a log-log scale (which expands the calibration result for small concentrations of CO). As demonstrated, the agreement between the calibration results for each channel is excellent. The surprising fact concerning the results of Fig. 1 is that the data were taken with the large beam waist, for which the irradiance-dependent exponent is 1.9. Indeed, calibrations taken on all occasions in the laminar flames faithfully give linear behavior for both the small beam waist ($b=1.2$) and the large beam waist ($b=1.9$). This does not necessarily mean that the behavior predicted by Eq. (8) is incorrect. For example, if the quenching rate does not change from point to point shown in the plots of Fig. 1, then the observed behavior would be expected.

Knowing the Raman and TPLIF calibration results, some typical data were reduced for the nonpremixed jet flame. The resulting CO concentrations are plotted conditionally against

temperature in Fig. 2. As shown, the Raman measurements of CO concentration show much less scatter than the corresponding TPLIF measurements. Again, there is very little difference in this regard between the signals obtained with a large beam waist or a small beam waist. Both channels exhibit scatter that is significantly larger than that obtained in the calibration process, such that the scatter in Fig. 2 results, in part, from flame fluctuations. The anomalously large scatter

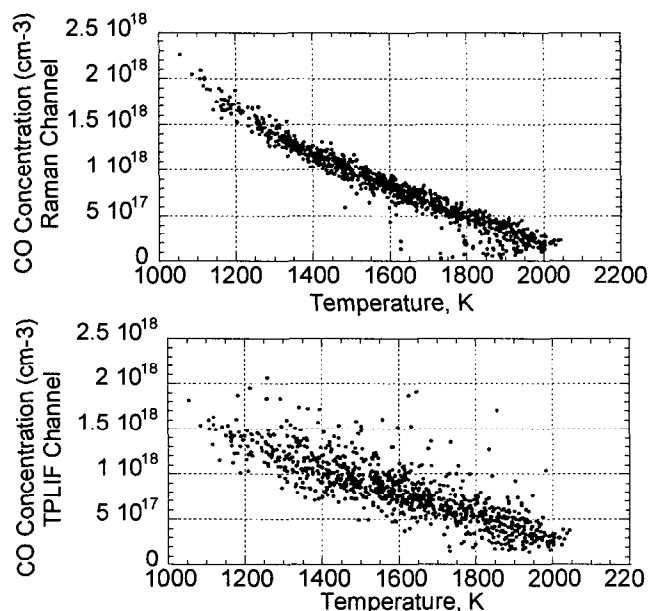


Figure 2. Simultaneous CO concentrations obtained using Raman scattering (upper plot) and TPLIF (lower plot) in a nonpremixed, $H_2/CO/N_2$ jet flame.

for the TPLIF channel is typical of data obtained for these flame conditions, as verified by reducing over 50,000 shots of data taken on numerous occasions. While the scatter of the data for the TPLIF and Raman channels differs greatly, a running mean value vs. temperature agrees well for both channels. There is a slight discrepancy between CO Raman and TPLIF results obtained for temperatures below 1400 K. This may arise from inadequate correction for the Boltzman fraction variation with temperature. One possible cause is an inadequate computation of spectral overlap. For example, we have recently learned that we underestimated the influence of photoionization broadening (Di Rosa and Farrow, 1999). The calibration data of Figure 1 were obtained over a limited temperature range.

Typical results obtained for the methane-air bluff-body burner are shown in Fig. 3. The behavior in this turbulent flame is substantially different than that observed in Fig. 2. In fact, the spread in the CO concentration measured using the TPLIF technique is *smaller* than that for the corresponding Raman scattering channel. Moreover, data taken using the small beam waist exhibits significantly less scatter than the

corresponding data taken with a large beam waist. It is therefore not surprising that subsequent data taken in hydrocarbon-fueled turbulent flames has been of great utility (Barlow and Frank, 1998). Nevertheless, the anomalous scatter exhibited in the results of Fig. 2 is driving us to examine several issues in greater detail during future studies.

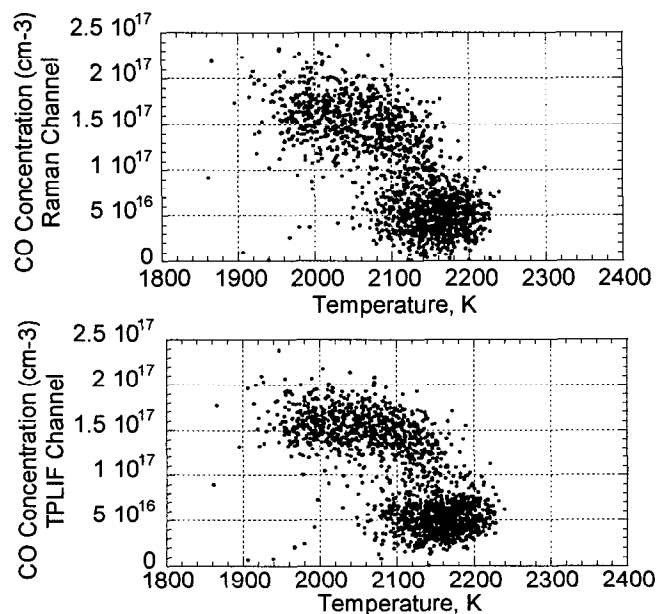


Figure 3. Simultaneous CO concentrations obtained using Raman scattering (upper plot) and TPLIF (lower plot) in a premixed, methane-air bluff-body burner.

FUTURE INVESTIGATIONS

Based on the experimental results described in this manuscript, we are presently pursuing several possible explanations for the anomalous scatter observed in nonpremixed jet flames of $H_2/CO/N_2$ fuel. For example, beam steering effects could differ between the two flames. To test this, a pinhole is placed after the test section, followed by a photodiode. The rms deviation of the photodiode is measured both with and without a flame for both turbulent flame conditions studied in this paper. No significant difference is observed between the two cases. Another possible explanation is the difference in beam waists between the Raman instrument (800 μm) and the TPLIF instrument (260 μm). Because of the nonlinear nature of the two-photon absorption utilized in the present experiments, the differences between the beam waists for the Raman and TPLIF systems will be amplified (Wirth and Fatunmbi, 1990). To test this effect, TPLIF data has been obtained for both small and large beam waists, as described in this paper. The spread in the data obtained using the large beam waist is similar to that for the small beam waist in the $H_2/CO/N_2$ flames. Unfortunately, it is possible that two

different effects are influencing the comparison between the data for the two laser beam diameters; for example, the lower irradiance that results when using a large beam waist will tend to increase the dependence of the TPLIF signal on collisional quenching (in accordance with Eq. (8)) while reducing any potential signal variations caused by the difference in spatial resolution from the Raman system.

To answer questions about the reduction in quenching effects as a function of laser irradiance, particularly when considering such issues as the spatial and temporal distribution of laser-pulse irradiance, we are also pursuing a more detailed rate-equation analysis of the TPLIF signal. There are other reasons for pursuing a more detailed explanation of the excitation dynamics involved in obtaining TPLIF signals; for example, a *sublinear* irradiance-dependent exponent is obtained (Everest et al, 1996), in conflict with the simple result given by Eq. (7). In addition, recent interest in the rate-equation study has resulted because the cross sections that are necessary for such an undertaking have recently been measured by Di Rosa and Farrow (1999) using high-resolution spectroscopy. Another possible explanation for an anomalously large spread in TPLIF measurements of CO concentration could be photodissociation of vibrationally excited CO₂ to form additional CO, as has been reported recently by Nefedov (1998). This process could be particularly important for flame regions where CO concentrations are comparatively small. We presently have an extensive amount of temperature data that were obtained simultaneously with concentration measurements of CO and CO₂. We plan to use these results to assess the importance of the effects highlighted by Nefedov et al. (1998).

CONCLUSIONS

An experimental study of TPLIF measurements of CO has been accomplished using simultaneously obtained results from a Rayleigh/Raman scattering instrument. Comparisons in laminar, premixed methane-air flames and laminar, nonpremixed H₂/CO/air flames yielded excellent agreement with CO concentrations obtained using Raman scattering. In addition, favorable single-shot pdf results were obtained in a turbulent, premixed, methane-air bluff-body burner. However, an anomalously large spread in single-shot CO concentration data was observed in a nonpremixed H₂/CO/N₂ jet flame.

ACKNOWLEDGEMENTS

This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, and by U. S. Air Force Contracts F33615-95-C-2507, F33615-97-C-2702, and F33615-92-C-2202. The authors wish to thank J. H. Frank, J. R. Gord, M. D. Di Rosa, R. L. Farrow, and Q. V. Nguyen for helpful discussions concerning two-photon experiments. The authors also wish to thank K. C. Smyth and P. J. H. Tjossem for

providing information concerning the spectroscopy of the X¹Σ⁺–B¹Σ⁺ electronic transition of CO. The authors are grateful for the assistance of Tom Prast in constructing the experimental apparatus.

REFERENCES

- Aldén, M., Wallin, S., and Wendt, W., 1984, "Applications of Two-Photon Absorption for Detection of CO in Combustion Gases," *Appl. Phys. B*, Vol. 33, pp. 205-208.
- Bamford, D. J., Jusinski, L. E., and Bischel, W. K., 1986, "Absolute Two-Photon Absorption and Three-Photon Ionization Cross Sections for Atomic Oxygen," *Phys. Rev. A*, Vol. 34, pp. 185-198.
- Barlow, R. S., 1996, "Proceedings of the International Workshop on Measurement and Computation of Turbulent Nonpremixed Flames," Sandia Report SAND96-8564-UC-1409, Sandia National Laboratories, Albuquerque, New Mexico. For more recent information, visit www.ca.sandia.gov/tdf/Workshop.html.
- Barlow, R. S., and Carter, C. D., 1994, "Raman/Rayleigh/LIF Measurements of Nitric Oxide Formation in Turbulent Hydrogen Flames," *Combustion and Flame*, Vol. 97, pp. 261-280.
- Barlow, R. S., and Carter, C. D., 1996, "Relationships Among Nitric Oxide, Temperature, and Mixture Fraction in Hydrogen Jet Flames," *Combustion and Flame*, Vol. 104, pp. 288-299.
- Barlow, R. S., Fiechtner, G. J., and Chen, J.-Y., 1996, "Oxygen Atom Concentrations and NO Production Rates in a Turbulent H₂/N₂ Jet Flame," Twenty-Sixth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA., pp. 2199-2205.
- Barlow, R. S., and Frank, J. H., 1998, "Effects of Turbulence on Species Mass Fractions in Methane/Air Jet Flames," accepted for publication, Twenty-Seventh Symposium (International) on Combustion, Pittsburgh, PA.
- Barlow, R. S., Fiechtner, G. J., Carter, C. D., and Chen, J.-Y., 1999, "Experiments on the Scalar Structure of Turbulent CO/H₂/N₂ Jet Flames," *Combustion and Flame*, in preparation.
- Bernstein, J. S., 1991, "Laser Ionization Studies of Hydrocarbon Flames," Ph. D. Dissertation, Cornell University, Ithaca, NY.
- Chen, J.-Y., Kollmann, W., and Dibble, R. W., 1989, "PDF Modeling of Turbulent Nonpremixed Methane Jet Flames," *Combustion Science and Technology*, Vol. 64, pp. 315-346.
- Chen, J.-Y., and Dibble, R. W., 1991, "A Perfectly-Stirred Reaction Description of Chemistry in Turbulent Nonpremixed Combustion of Methane in Air," *Combustion Science and Technology*, Vol. 84, pp. 45-50.
- Correa, S. M., and Gulati, A., 1988, "Non-Premixed Turbulent

- CO/H₂ Flames at Local Extinction Conditions," Twenty-Second Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA., pp. 599-606.
- Correa, S. M., and Gulati, A., 1992, "Measurements and Modeling of Bluff Body Stabilized Flame," *Combustion and Flame*, Vol. 89, pp. 195-213.
- Correa, S. M., Gulati, A., and Pope, S. B., 1994, "Raman Measurements and Joint PDF Modeling of a Nonpremixed Bluff-Body-Stabilized Methane Flame," Twenty-Fifth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA., pp. 167-1173.
- Di Rosa, M. D., and Farrow, R. L., 1999, "Cross Sections of Photoionization and AC Stark Shift Measured from Doppler-Free B-X(0,0) Excitation Spectra of CO," accepted for publication, *Journal of the Optical Society of America B*.
- Eberly, J. H., 1979, "Extended Two-Level Theory of the Exponential Index of Multiphoton Processes," *Phys. Rev. Lett.*, Vol. 42, pp. 1049-1052.
- Everest, D. A., Shaddix, C. R., and Smyth, K. C., 1996, "Quantitative Two-Photon Laser-Induced Fluorescence Imaging of CO in Flickering CH₄/Air Diffusion Flames," Twenty-Sixth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, pp. 1161-1169.
- Fiechtner, G. J., and Barlow, R. S., 1999, "The Irradiance-Dependent Exponent: Implications for the Application of Two-Photon Laser-Induced Fluorescence of CO in Flames," in preparation.
- Fiechtner, G. J., Carter, C. D., Frank, J. H., and Barlow, R. S., 1999, "Simultaneous Measurements of CO Concentration in Turbulent Flames using Two-Photon Laser-Induced Fluorescence and Raman Scattering," in preparation.
- Goorvitch, D., 1994, "Infrared CO Line List for the X¹Σ⁺ State," *The Astrophysical Journal Supplement Series*, Vol. 95, pp. 535-552.
- Hauman, J., Seitzman, J. M., and Hanson, R. K., 1986, "Two-Photon Imaging of CO in Combustion Flows Using Planar Laser-Induced Fluorescence," *Optics Letters*, Vol. 11, pp. 776-778 (1986).
- Hancock, R. D., Bertagnolli, K. E., and Lucht, R. P., 1997, "Nitrogen and Hydrogen CARS Temperature Measurements in a Hydrogen/Air Flame Using a Near-Adiabatic Flat-Flame Burner," *Combustion and Flame*, Vol. 109, No. 3, pp. 323-331.
- Lucht, R. P., 1987, "Applications of Laser-Induced Fluorescence Spectroscopy for Combustion and Plasma Diagnostics," in *Laser Spectroscopy and Its Applications*, L. J. Radziemski, R. W. Solarz and J. A. Paisner, eds., Marcel Dekker, Inc., New York, NY.
- Mauß, F. Keller, D., and Peters, N., 1990, "A Lagrangian Simulation of Flamelet Extinction and Re-Ignition in Turbulent Jet Diffusion Flames," Twenty-Third Symposium on Combustion, The Combustion Institute, Pittsburgh, PA, pp. 693-698.
- Masri, A. R., and Dibble, R. W., 1988, "Spontaneous Raman Measurements in Turbulent CO/H₂/N₂ Flames Near Extinction," Twenty-Second Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA., pp. 607-618.
- Masri, A. R., Dibble, R. W., and Barlow, R. S., 1992, "Raman-Rayleigh Measurements in Bluff-Body Stabilised Flames of Hydrocarbon Fuels," Twenty-Fourth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA., pp. 317-324.
- Masri, A. R., Dibble, R. W., and Barlow, R. S., 1996, "The Structure of Turbulent Nonpremixed Flames Revealed by Raman-Rayleigh-LIF Measurements," *Progress in Energy and Combustion Science*, Vol. 22, pp. 307-362.
- Mokhov, A. V., Levinsky, H. B., van der Meij, C. E., and Jacobs, R. A. A. M., 1995, "Analysis of Laser-Induced-Fluorescence Carbon Monoxide Measurements in Turbulent Nonpremixed Flames," *Applied Optics*, Vol. 34, pp. 7074-7082.
- Nefedov, A. P., Sinel'shchikov, V. A., Usachev, A. D., Zobnin, A. V., 1998, "Photochemical Effect in Two-Photon Laser-Induced Fluorescence Detection of Carbon Monoxide in Hydrocarbon Flames," *Applied Optics*, Vol. 37, No. 33, pp. 7729-7736.
- Nguyen, Q. V., and Paul, P. H., 1996, personal communication.
- Nguyen, Q. V., Dibble, R. W., Carter, C. D., Fiechtner, G. J., and Barlow, R. S., 1996, *Combustion and Flame*, Vol. 105, pp. 499-510.
- Salmon, J. T., Jr., and Laurendeau, N. M., 1990, "Relative Fluorescence-Quenching Measurements of Atomic Hydrogen in Subatmospheric H₂/O₂/N₂ Flames with Photoionization Controlled-Loss Spectroscopy," *Journal of Quantitative Spectroscopy and Radiative Transfer*, Vol. 43, p. 155.
- Saxon, R. P., and Eichler, J., 1986, "Theoretical Calculation of Two-Photon Absorption Cross Sections in Atomic Oxygen," *Phys. Rev. A*, Vol. 34, pp. 199-206.
- Seitzman, J. M., Haumann, J., and Hanson, R. K., 1987, "Quantitative Two-Photon LIF Imaging of Carbon Monoxide in Combustion Gases," *Applied Optics*, Vol. 26, pp. 2892-2899.
- Van Oostendorp, D. L., Borghols, W. T. A., and Levinsky, H. B., 1991, "The Influence of Ambient Air Entrainment on Partially Premixed Burner Flames: LIF Imaging of CO and OH," *Combustion Science and Technology*, Vol. 79, pp. 195-206.
- Wirth, M. J., and Fatunmbi, H. O., 1990, "Very high Detectability in Two-Photon Spectroscopy," *Analytical Chemistry*, Vol. 62, pp. 973-976.